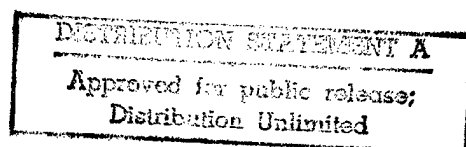


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Massive Data Storage Utilizing STM Technology:Storage Medium

Technical Abstract:

Digital mass storage devices built on scanning tunneling microscope technology can result in storage densities of 10^{12} bits/cm². In the STM based mass storage device electrons emitted from a microtip cause a physical change in a storage medium's surface. Current densities between the microtip and storage medium can be as high as 10^6 amps/cm² and electric fields can be as large as 10^6 V/cm. It is anticipated that this new type of mass storage subsystem will have megahertz transfer rates and access times of several milliseconds per gigabyte.

The objective of this SBIR Phase I contract is to evaluate potential storage media for read/write mass storage device utilizing STM technology. Several gas/solid, liquid/solid and solid system were evaluated for the storage medium. Storage media that show exceptional promise are magnetic materials, quantum structures, and electrochemical solutions.

We conclude from this SBIR phase I research effort that it is possible to develop a read/write mass storage device from STM technology. There are several storage media that can be utilized; however, experiments must be performed to select the optimal storage medium. The level of effort required to successfully complete this research project is estimated at 10 man years. Because the SBIR program provides funding for projects requiring 4 - 5 man years, QuanScan will pursue funding for this research project from sources outside the SBIR program.

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a. Introduction

Magnetic based mass storage devices have storage densities of 10^6 bits/cm² and optical based mass storage devices have densities of 10^8 bits/cm². Future developments in these technologies might result in an order of magnitude improvement or storage densities approaching 10^9 bits/cm². Future military missions in BMC³ require mass storage subsystems with far greater capacities. Table 1 compares the optical and magnetic mass storage devices with the STM based mass storage devices.

	Magnetic	Optical	Tunneling(1)
	-----	-----	-----
\$/Byte(2)	4 x 10E-6	5 x 10E-6	1 x 10E-9
Archival Life	2 - 3 yrs	10 yrs	> 10 yrs
Store Density	.0025 gb/ sq cm	.025 gb/ sq cm	440 gb/ sq cm
Access Time	40 msec	250 msec	15 msec
Medium Size (1 GB)	100-3.5 in disks	1-5.24 in disk	1-.078 in square
Drive Size	4x6x2 in	6x7x2 in	1x1x1 in
Controller	One card	One card	One card

Table 1

It is demonstrated that the electrons from a microtip in a scanning tunneling microscope can generate a permanent mark on a surface. For example, 500 angstrom diameter marks have been generated on several materials such as Si:H, metallic glasses, and gold. By creating permanent marks on a surface it is feasible to develop a write once read many (WORM) type mass storage subsystem. Figure 1 illustrates nine submicron bits that were written on a thin metal film at QuanScan.

This SBIR Phase I study examines the feasibility of producing a read/write mass storage device utilizing STM technology. Specifically, the project focusses on the identification of several possible physical system that may serve as the storage medium in an STM based read/write mass storage subsystem. Initially, storage media utilized for read/write optical disks such as chalcogenide glasses and electric charge systems will be studied. Once identified, the most promising storage media will be developed during the SBIR Phase II research.

a.1. Examples of SPM

Scanning probe microscopy permits the submicron imaging of surface features in ambient air and liquids. Figure 1 illustrates the commercial STM manufactured and sold by QuanScan. It is comprised of a personal computer, an electronic control unit, and a microscope stage.

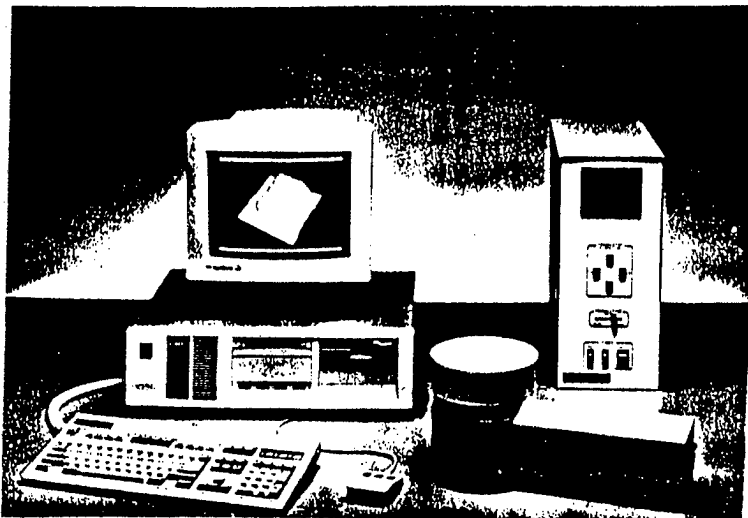


Figure 1

The scanning probe microscope is useful for observing the microstructure of materials as illustrated in Figure 2 through 4.

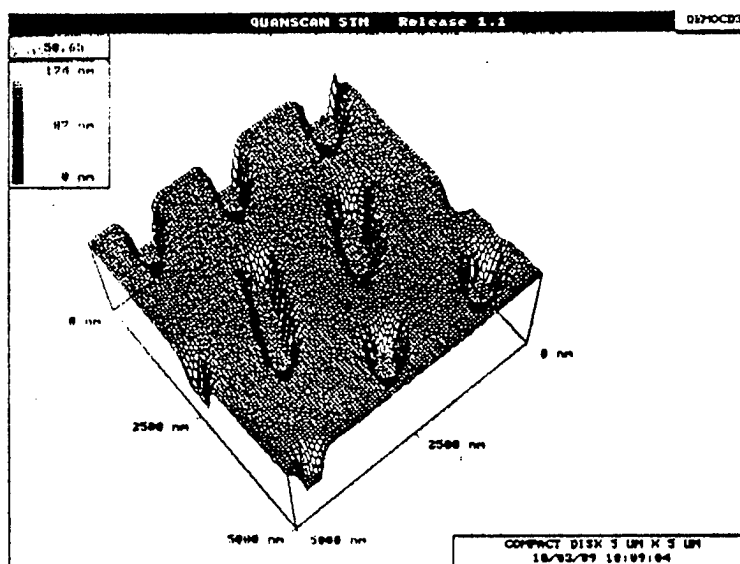


Figure 2

STM image of bits on a commercial compact disk, each bit is .1 micron deep and .8 micron wide.

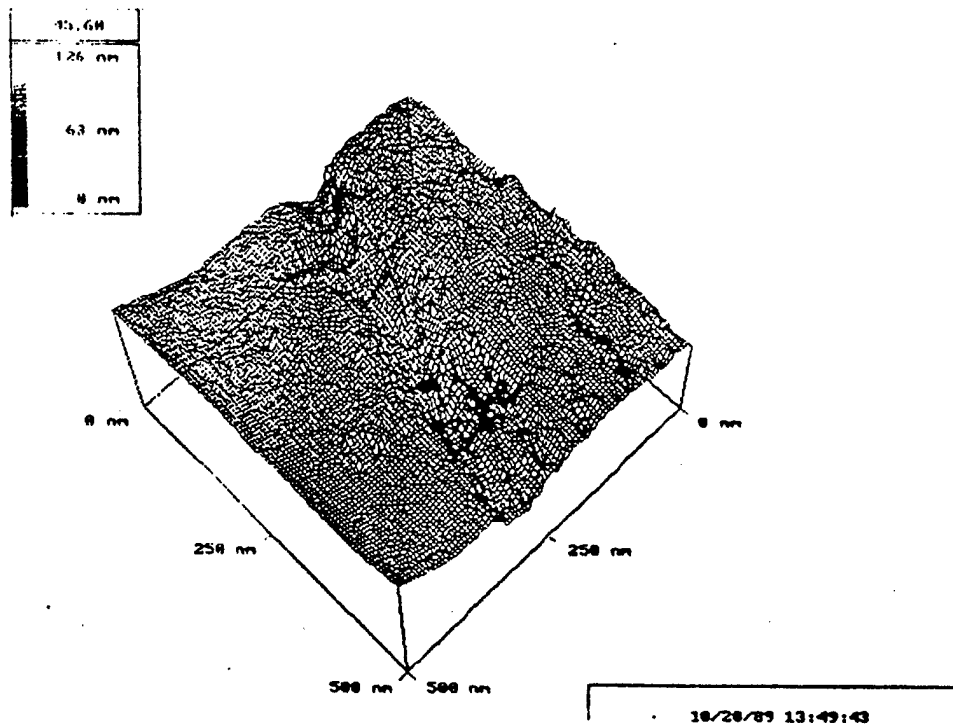


Figure 3

Atomic force microscope image of a surface microcrack in a piece of plastic. The crack is 250 angstroms wide and only a few nanometers deep.

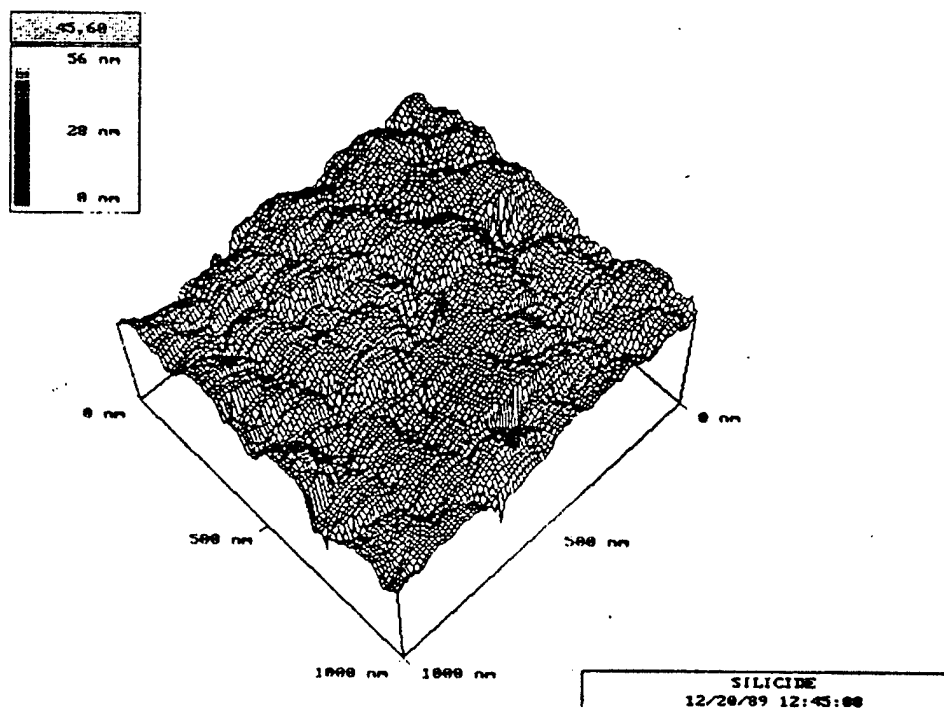


Figure 4

STM image grain boundaries on a silicide. From the STM image grains as small as .1 micron in diameter are detected.

a.2. General Introduction

A recent development in instrumentation has made possible the nondestructive, noncontact measurement of surface topography to unprecedented resolutions. These instruments are based on interaction of a sharp probe and the sample surface and are called Scanning Probe Microscopes (SPM). The SPMs are based on the Scanning Tunneling Microscope (STM) which was invented by R. Young in 1972¹. The instrument was further refined by Binig and Rohrer² and used for atomic resolution imaging of surfaces of conducting and semiconducting materials.

STM is based on the quantum mechanical tunneling of electrons from a sharp metallic electrode (the tip) to a second electrode (the sample) under an applied electric field. The sample is usually stationary while the tip is scanned over the sample. The tip is mounted on piezoelectric ceramic materials³ and is capable of moving in the x, y, and z directions by the application of electric fields to the ceramics. The ceramics are capable of high resolution movements from .1Å to 100 microns.

A potential is applied to the z-ceramic through a feedback control unit, such that, the tip-to-sample current remains constant. In this mode, the tip follows the topography of the surface.

The vertical resolution of the instrument is due to the strong dependence of the tunneling current on the tip-sample spacing. A simple relation for the tunneling current density is given by:

$$J = A*(V/d)*\exp(-a*d)$$

where d is the tip-sample spacing, V is the applied voltage, and A and a are constants. If the tip-sample spacing is changed by 1 Å (10⁻¹⁰ meters), the tunneling current changes by an order of magnitude. This follows from the exponential dependence of the tunneling current density on the tip-sample spacing. The lateral resolution of the instrument depends on

¹ R. Young, J. Ward, and F. Scire, Rev. Sci. Inst., 43, 999 (1972).

² G. Binnig, C. F. Quate, and Ch. Gerber, and E. Weibel, Phys. Rev. Lett., 50 120 (1983).

³ Piezoelectric ceramics are materials which change physical dimensions upon excitation by an electric potential. For example, a piezoelectric ceramic tube will expand along its length by 100 Å (depending on its physical dimensions) by application of 1 volt between its inner and outer electrodes.

the tip geometry and the above equation. By proper tip preparation technique, spatial resolution of less than .1Å can be obtained.

A feedback loop is used to maintain a constant tip-sample spacing while the tip is being scanned over the surface. The block diagram of the STM feedback is shown in Figure 1. The feedback electronics operate as follows:

- a. Under an applied voltage to the tip, the electrons tunnel from the tip to the sample resulting in a current flow.
- b. A current-to-voltage converter outputs a voltage, V_{out} , which is proportional to the tunneling current.
- c. V_{out} is then compared to a reference voltage, V_{ref} , in the comparator.
- d. The output of the comparator activates the z-direction piezoelectric ceramic, p_z , which maintains a constant tip-to-sample current.

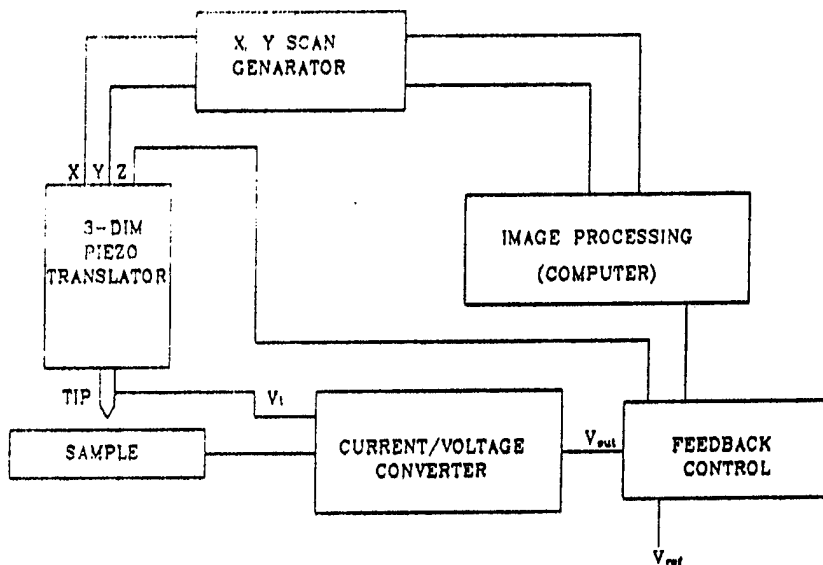


Figure 5

After the tip is brought into a feedback position near the surface, it is scanned using the x- and y-direction piezoelectric ceramics. The tip maintains a constant distance (constant current) from the sample as it follows the contours of the surface. The voltage to the z-piezoelectric, which is used to maintain a constant tip-to-sample spacing is now proportional to the topography of the surface. The image is digitized and stored in the computer for further analysis.

The STM has been applied as a surface probe to investigate surface properties of materials in vacuum⁴, air,⁵ and solutions.⁶ The applications range from imaging of biological molecules⁷ to atomic resolution studies on semiconducting surfaces.⁸

The STM is limited to the applications where the samples are conductive or semiconducting. For insulating samples, the Atomic Force Microscope (AFM) is used. The AFM is based on technologies of the STM and is capable of imaging insulating materials with atomic resolution.

The AFM, invented by Binnig, Quate, and Gerber,⁹ is based on the motion of a cantilever over the surface. A tip is mounted on the cantilever which is brought close to the surface. The tip and the cantilever are mounted on piezoelectric ceramics for fine motion in the x, y and z directions (Figure 2). The van der Waals force between the tip and the sample results in the deflection of the cantilever. The deflection of the cantilever is detected through a high resolution displacement sensor. As the tip and the cantilever are scanned over the surface, the deflection of the cantilever and therefore the force between the tip and the sample are kept constant through a feedback loop. The feedback loop is the same as the case of the STM. For the AFM, the signal from the displacement sensor is used instead of the tunneling current in the feedback loop.

The dimensions of the cantilever are selected such that it deflects 10 to 1000 Angstroms under a force of 10^{-11} to 10^{-8} Newtons which is the same order of magnitude as van der Waals force. The small force exerted by the tip on the cantilever does not alter the surface of the materials.

⁴ R. S. Becker, J. A. Golovchenko, and B. S. Swartzentruber, Phys. Rev. Lett., 54, 2678 (1985).

⁵ J. Jahanmir, P.E. West, S. Hsieh, and T. N. Rhodin, J. Appl. Phys.,

⁶ J. Schneir, R. Sonnenfeld, P. K. Hansma, and J. Tersoff, Phys. Rev. B, 34, 4979 (1986) and S. Morita, S. Tsukada, and N. Mikoshiba, Jap. J. Appl. Phys. 26, L306 (1987).

⁷ D. C. Dahn, M. O. Watanabe, B. L. Blackford, M. H. Jericho, and T. J. Beveridge, J. Vac. Sci. Technol. A6, 548 (1988).

⁸ R. M. Feenstra and A. P. Fein, Phys. Rev. B, 32, 1394 (1985).

⁹ G. Binnig, C. F. Quate, and Ch. Gerber, Phys. Rev. Lett. 56, 930 (1986).

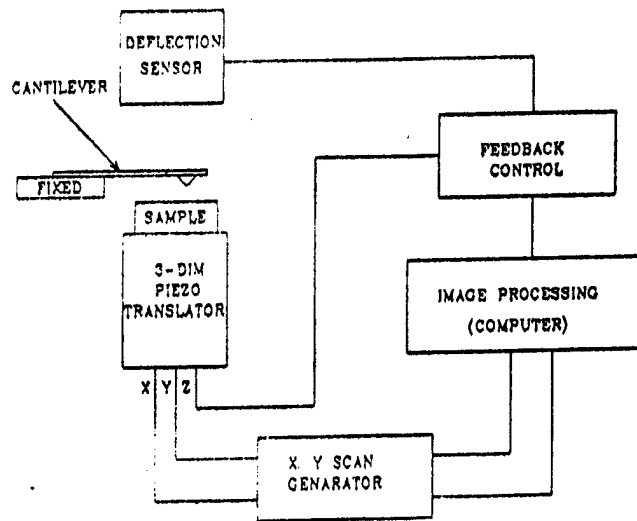


Figure 6

b. Phase I Research

Several of the materials listed in the Phase I research plan were evaluated and eliminated as potential storage media. The storage media substrates that were selected are quantum structure substrates, electrochemical substrates, and thermo-magnetic substrates.

There is considerable uncertainty in the development of the STM based mass storage system because the bit sizes are an order of magnitude less than the bits used in existing mass storage devices.

In the following sections these substrate systems are described.

b.1. Quantum Structure Substrate

Because a current is required for the operation of the scanning tunneling microscope the microscope can be used to place small amounts of charge in metallic section imbedded in an insulating film at the substrate surface. This approach is similar to the IGFET described by Sze¹⁰. Figure 7 illustrates the difference between a bit "0" and a bit "1" state in the quantum structure memory.

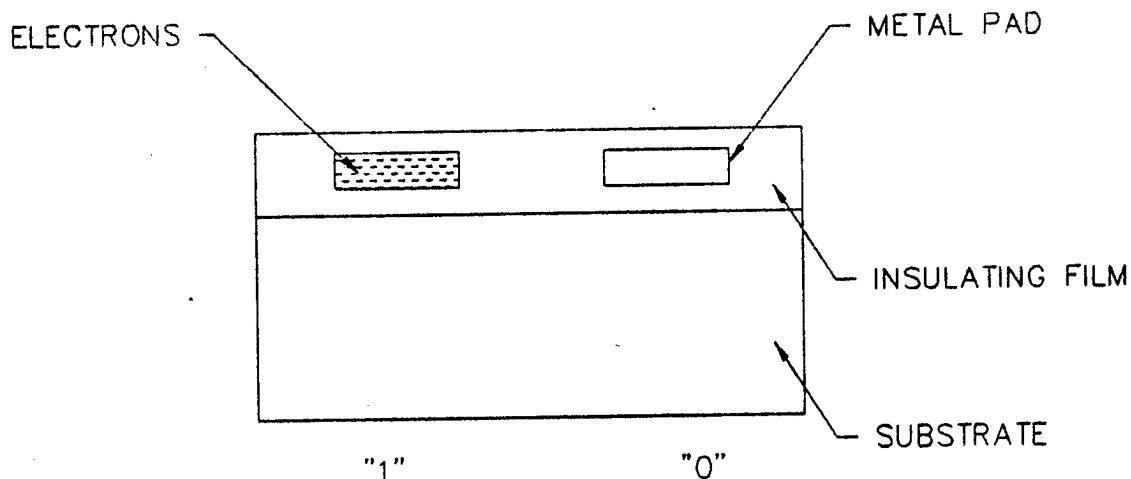


Figure 7

A bit is written and erased by reversing the bias between the probe tip and the underlying substrate, see figure 8.

¹⁰ Physics of Semiconductor Devices, S.M. Sze, John Wiley & Sons, NY, 1969

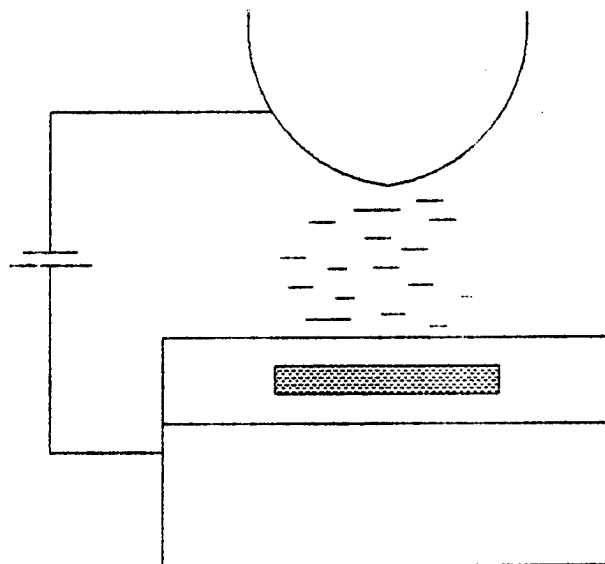


Figure 8

The potential energy diagram for this type of structure is given in Figure 9. In this diagram electrons must tunnel through the thin insulating film and become trapped in the metal electrode.

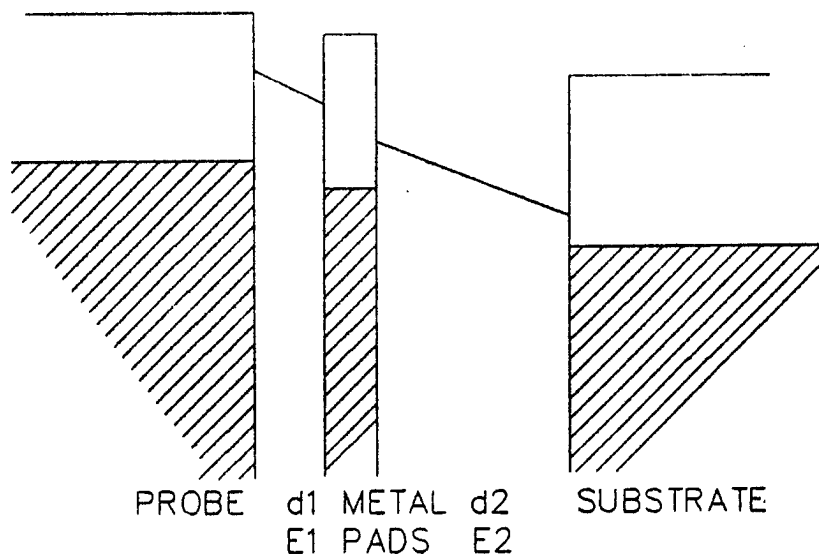


Figure 9

A bit is read by read with a small metal probe in the end of a metal cantilever. The cantilever deflects as it passes over bit having a charge. Using a technique similar to the atomic force microscope the motion of the cantilever is measured with a one dimensional scanning tunneling microscope. Illustrated in Figure 10 is the entire read/write/erase head.

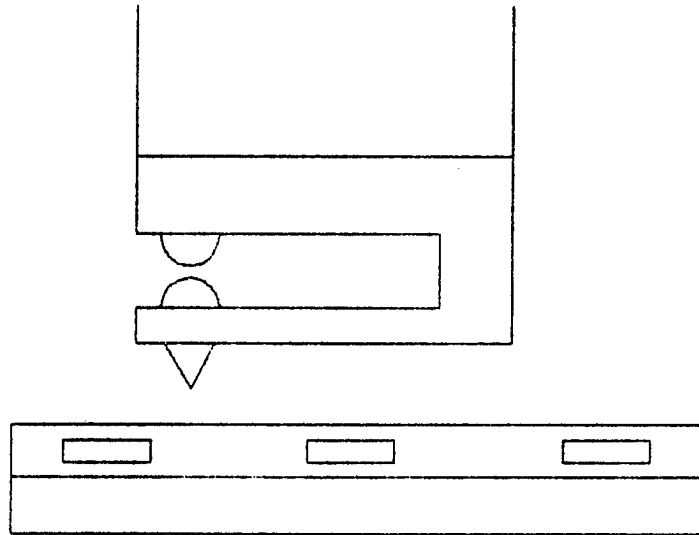


Figure 10

b.1.1. Specific Example

There are several possible structure that can be envisioned for the Quantum structure storage media. The structure illustrated in Figure 11 is ideal for demonstrating this concept.

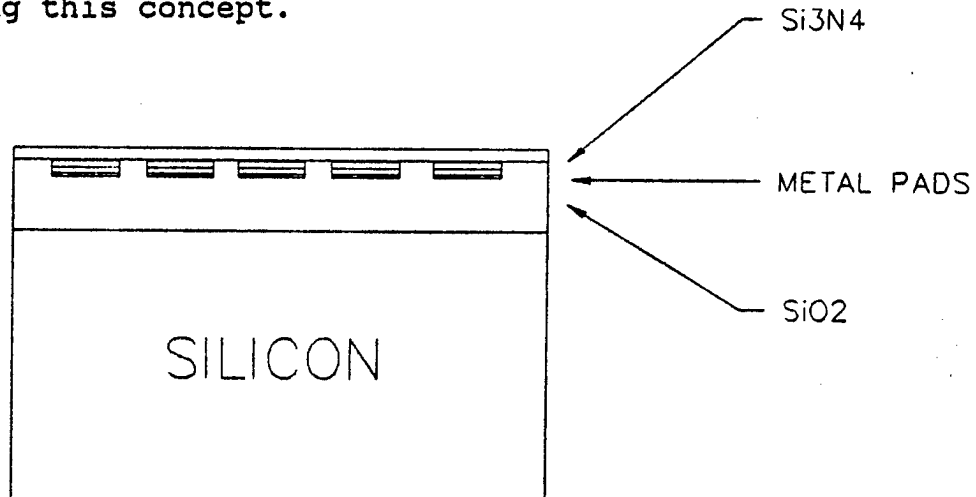


Figure 11

Such a structure can be fabricated by growing a thick oxide layer, approximately 1000 angstroms, on a metal substrate. Using electron beam lithography, and reactive ion etching techniques, holes of 100 - 500 angstroms deep, and 300 - 1000 angstroms in diameter are etched in the oxide film. A process is undertaken to fill the holes with a metal, and then a thin oxide or nitride layer is developed. The amount of leakage from the metal pads in this structure is unknown and must be established.

b.1.2. Write/read times

Write/erase

The write and erase times in the Quantum memory are limited by the amount of time it takes to get a charge into and out off the metal pads. The relationship between the stored charge Q , and write/erase time when a step function V is applied between the substrate and the probe is given by:

$$Q(t) = Jdt$$

For Fowler-Nordheim field emission, the current density is:

$$J = AE^2 \exp(-E_0/E)$$

For a Schottky or Frankel-Poole type emission the current density follows the form:

$$J = BE \exp[-q(\phi_B - qE/\pi E_1)/kT]$$

The electric field in the thin insulator is a function of the applied voltage V and $Q(t)$:

$$E = V/(d_1 + d_2(\epsilon_1/\epsilon_2) - Q/(\epsilon_1 + \epsilon_2(d_1/d_2)))$$

In order to fully understand the write/erase time of the quantum memory the preceeding equations must be solved as a function of time. When solved we find that during the write process initially the stored charge increases linearly with time, becomes exponential, and then saturates. The field in the thin insulator decreases as the stored charge increases.

The upper limit for the write/erase time is calculated by assuming that the field remains constant throughout the write process and that the electron transport mechanism is field emission. A charge of 10^3 electrons will be deposited in .01 microsecond.

Read

Bits are read in the Quantum memory by measuring the deflection in a cantilever that senses charge, in a similar manner to the atomic force microscope. The read time is then controlled by the rate at which a cantilever motion is detected. This is controlled by the force constant k and the lowest resonant frequency of the cantilever, f .

$$f^2 \propto wt^3 E/l^3 m$$

and:

$$k \propto mf^2$$

where:

w = Width of cantilever (meters)
t = Thickness of cantilever (meters)
l = Length of cantilever (meters)
E = Youngs modulus (Newtons/meter²)
m = Mass of the cantilever (kilograms)

The electrostatic force that must be measured is given by:

$$f = q^2/4\pi\epsilon_1r^2$$

where:

r = Spacing between the probe and pad (meters)
q = Electric charge (coulombs)
 ϵ_1 = Dielectric constant (farads/meter)

A force of 10^{-5} Newtons is realized if the distance, r, is 30 angstroms and q is for 10^3 electrons.

To achieve a data transfer rate of 10 megahertz the f_r must be greater than 10 megahertz and a force of 5 newtons must be measurable. A silicon cantilever having dimensions of 20 microns wide by 100 microns long by .15 micron thick will have a resonant frequency of 120 Mhertz and will move 1 micron under a force of 10^{-5} Newtons.

b.1.3. Advantages/Disadvantages

There are several advantages and disadvantages to the quantum structure substrate. The advantages include the use of exiting microfabrication methods for preparing the storage media, its ease of implementation, and the large forces associated with the charges. Possible disadvantages include the possibility of current leakage from the metal pads and the requirement for developing a durable probe at the end of a cantilever.

b.2. Electrochemical Substrates

Ions from a solution can be stored in a polymer substrate using an electrochemical cell. The regions of the polymer substrate where ions are stored have 1000 times more conductivity than regions where ions are not stored. Figure 12 illustrates the difference between a bit "0" and bit "1" state for the electrochemical substrate.

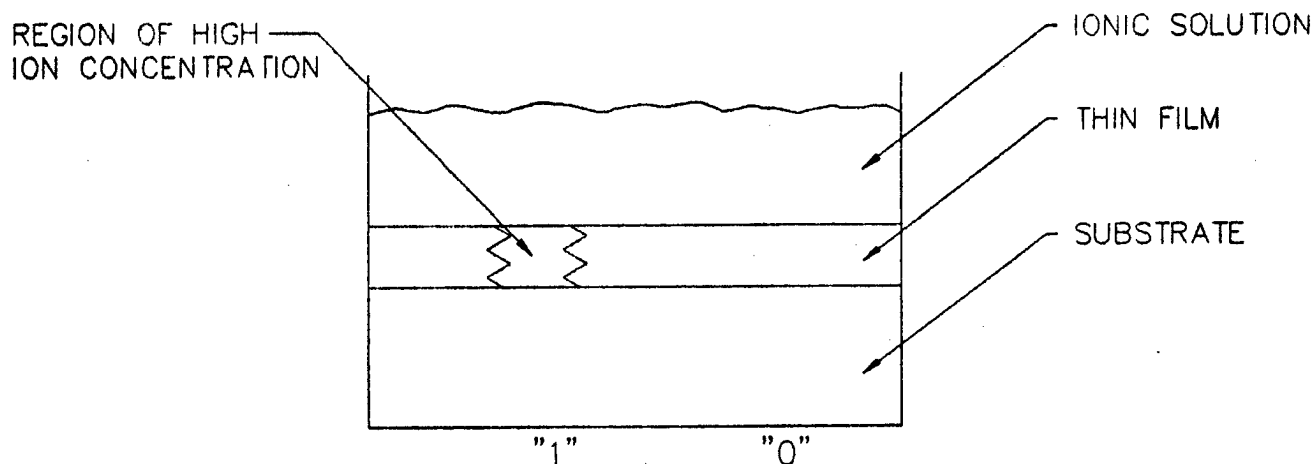


Figure 12

Figure 13 illustrates the potential energy diagram for the electrochemical substrate system. The presence of ions doped into the polymer film increases the barrier for the flow of electrons from the probe to the underlying substrate.

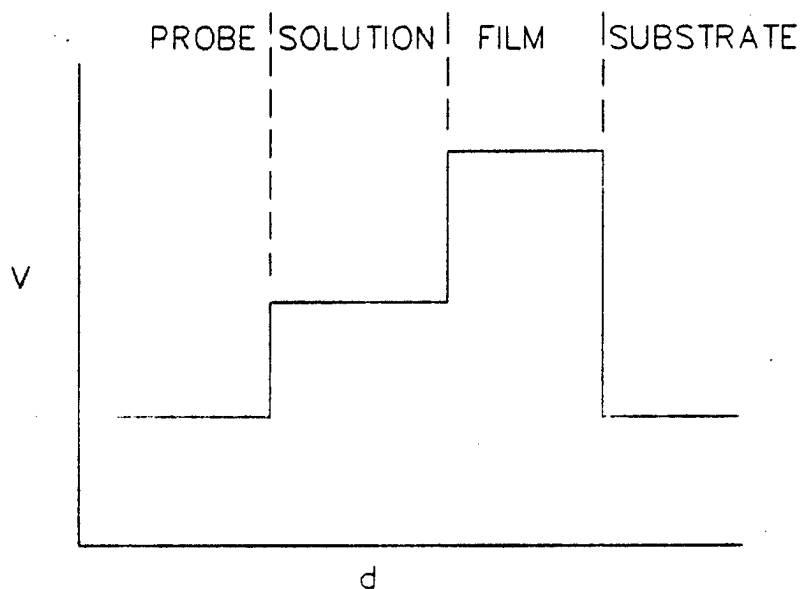


Figure 13

A bit is written on the substrate by electrochemically doping a small region of the polymer film. Doping of the polymer film electrochemically is a reversible process; thus, erasing a bit is achieved by reversing the bias between the probe tip and surface. A bit is read by measuring the flow of electrons between the probe tip and substrate.

b.2.1. Specific Example

Considerable research and development was undertaken to develop reversible electrochemical batteries from polymer materials¹¹. The material showing the greatest potential for a reversible electrochemical battery is polyacetylene. Polyacetylene can also be used for the storage media.

Conductive polymers are one-dimensional metallic systems. A prototype of these polymers is Polyacetylene. It is made of a single zigzag chain with a carbon atom on each corner. A proton is sitting on each carbon atom and every second carbon-carbon bond is a double bond. This is synthesized by polymerization of acetylene, Figure 14.

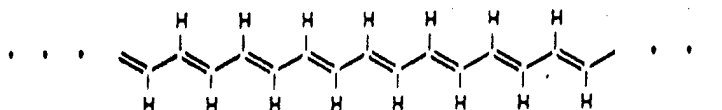


Figure 14

Also polyacetylene can be synthesized in a gedanken experiment by dehydration of polyethylene. This leads to a monoatomic one-dimensional crystalline lattice with repeat unit a . At each lattice site there is a CH-group and one electron. If this structure was stable, this electron would contribute to an energy band which is half filled, similar to an alkali metal. This structure is unstable at low temperatures and makes a metal-semiconductor transition. The transition is driven by the Peierls distortion and results in a biatomic superstructure: The atoms will group pairwise and alternating short and long interatomic distances will occur. In polyacetylene conjugated double bonds is formed (double bonds are shorter than single bonds). This results in a semiconducting material with a band-gap of 1.7 eV, Figure 15).

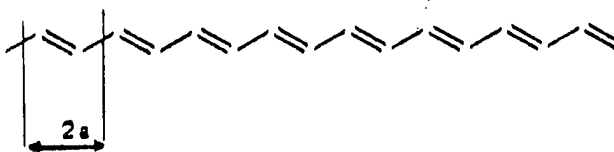
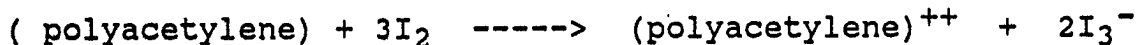


Figure 15

¹¹ J. Przyluski, M. Zagorska, Materials Science Forum, Vol. 21, (1987) pp31 -42.

The conductivity of this material can now be changed by doping. Doping changes the number of electrons on the polymer chain. The dopant itself has to be incorporated into the solid which is a three-dimensional effect. This effects the packing of the chains and the inter-chain reactions. A typical doping reaction is



The dopant sits as a counter-ion (I_3^-) on the polymer chain. The doping is carried out electrochemically: the electrons are withdrawn from the polymer or pushed into it at the electrodes and the counter-ions migrate from the electrolyte into the polymer in order atom maintain charge-neutrality. Some conductive polymers can be synthesized electrochemically, with the doping occurring simultaneously. In this case the polymer can be "dedoped" or compensated electrochemically.

The electrochemical process of doping reaction involve the oxidation (reduction) of the polymer chain with the introduction of a proper amount of anions (cations) stabilizing the polycarbonium cation (anion) formed:

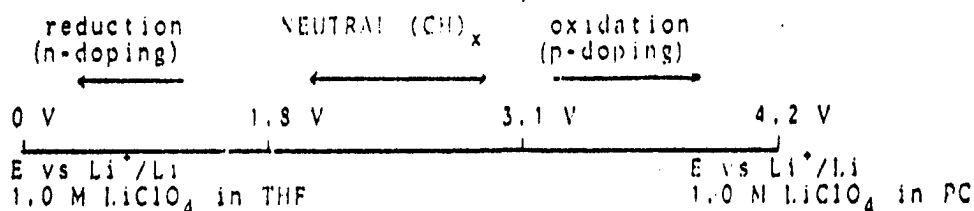
Oxidation at the anode (p-doping)



Reduction at the cathode (n-doping)



Electrochemical oxidation or reduction allows the control of the doping level in a more precise way than it is possible in typical chemical doping. The amount of charge passed is strictly related to the oxidation state of polyacetylene if $(\text{CH})_x$ is the only electrochemical species being oxidized or reduced. The electrochemical oxidation (or reduction) of polyacetylene occurs if higher (or lower) potential than potential of neutral $(\text{CH})_x$ is applied. The potential ranges required for the doping of trans- $(\text{CH})_x$ are:



The electrical conductivity can change from less than $0.1 \text{ (ohm-cm)}^{-1}$ to approximately $700 \text{ (ohm-cm)}^{-1}$. This is close to four orders of change in conductivity. Higher doping levels may be achieved in reduction reactions. Polyacetylene doping may be reversible depending on the type of dopant, type of the electrolyte and the conditions of electrolysis.

Figure 16 illustrates an approach for testing an electrochemical mass storage device.

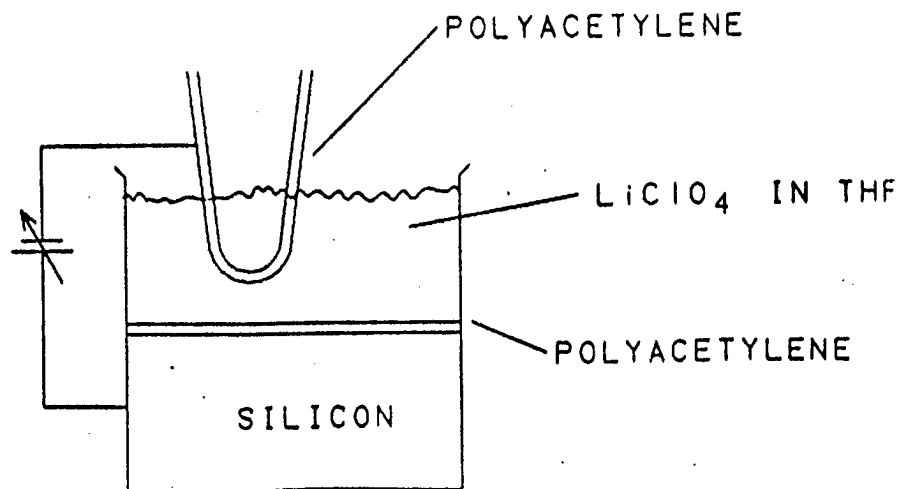


Figure 16

This approach, illustrated in Figure 16, will demonstrate the reversibility of the electrochemical reactions on a microscopic scale.

b.2.2. Read/write times

The read write times for an electrochemical storage medium must be determined experimentally. Estimates of the read/write time based on bulk properties are not useful because in the storage device only a thin film must absorb ions. All work reported previously deals with the storage of energy in bulk materials.

The reported work by Nagatomo et. al.¹² suggests that films of polyacetylene can be manufactured which are durable. Further Nagatomo cycled the films several thousand times with no degradation of the polyacetylene.

¹² T. Nagatomo, T. Honma, Ch. Yamamoto, K. Jegishi, O. Omoto, Jap. J. Phys., 22(1983) L 255 .

b.2.3. Advantages/Disadvantages

There are several advantages to an electrochemical substrate for the read/write storage medium. Advantages include the ability to prepare a storage medium that is extremely smooth, the chemical reaction occurring when a bit is stored or retrieved is relatively simple, and the potential low costs for the storage medium.

Disadvantages to the electrochemical approach include the requirement for a liquid and the lack of knowledge of the read write time for the storage medium.

b.3. Thermo-magnetic substrates

The current required for the operation of the scanning tunneling microscope can be used to heat small amounts of a surface. If the material is magnetic, then by applying a magnetic field across the storage medium a magnetic domain can be formed. The size of the domain will be approximately the same size as the surface area heated by the probe. This approach parallels the approach currently being used for erasable optical disks. Figure 17 illustrates the difference between a bit "0" and a bit "1" state in the thermo-magnetic memory.

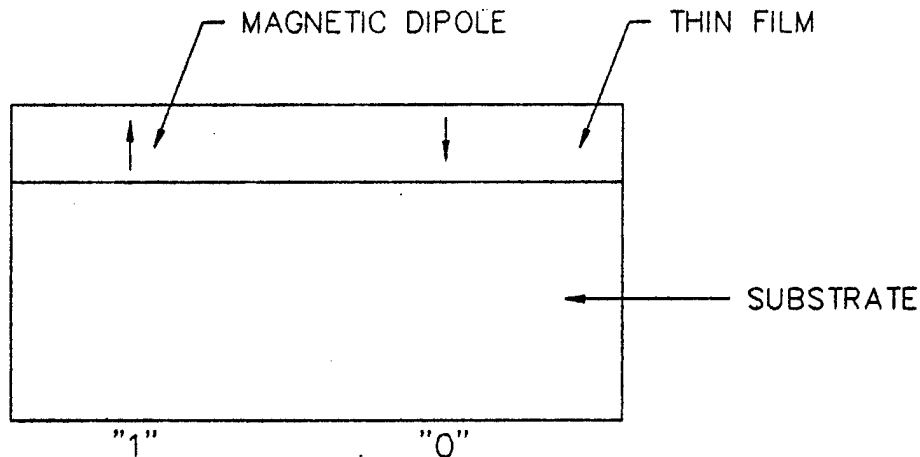


Figure 17

A bit is written and erased by reversing the magnetic field at the substrate's surface while the surface area is molton, see figure 18.

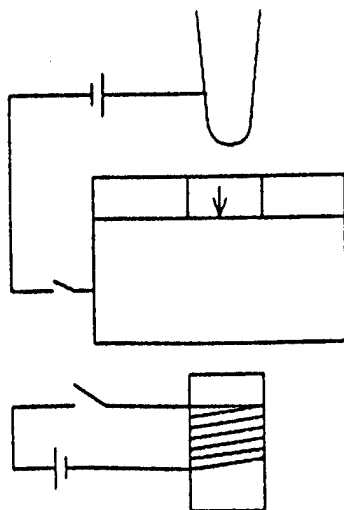


Figure 18

The potential energy diagram for this type of structure is given in Figure 19. Electrons heat the metal film as they pass through it.

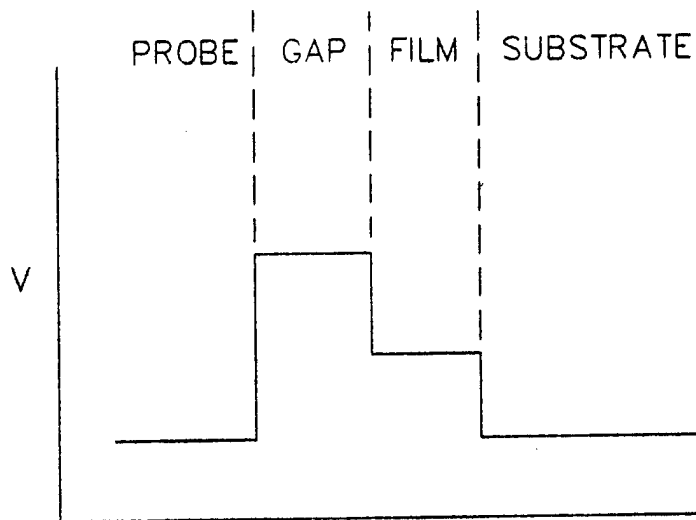


Figure 19

A bit is read with a small magnetic probe at the end of a cantilever. The cantilever deflects as it passes over bit with a magnetic domain. Using a technique similar to the atomic force microscope the motion of the cantilever is measured with a one dimensional scanning tunneling microscope. Illustrated in Figure 20 is the entire read/write/erase head.

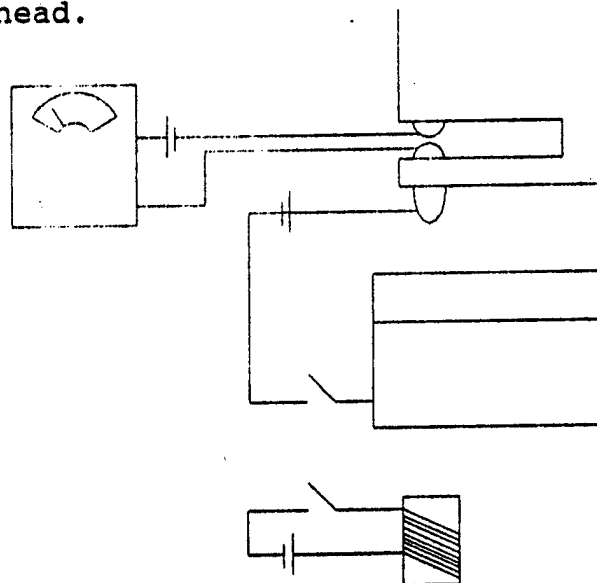


Figure 20

b.3.1. Specific Example

There are several possible materials that can be envisioned for the thermo-magnetic structure storage media. The structure illustrated in Figure 21 is ideal for demonstrating this concept. In fact Staufer et. al.¹³ have demonstrate an ability to write bits on this material.

¹³ U. Staufer, L. Scandella, R. Wiesendanger. Z. Phys. B., in press.

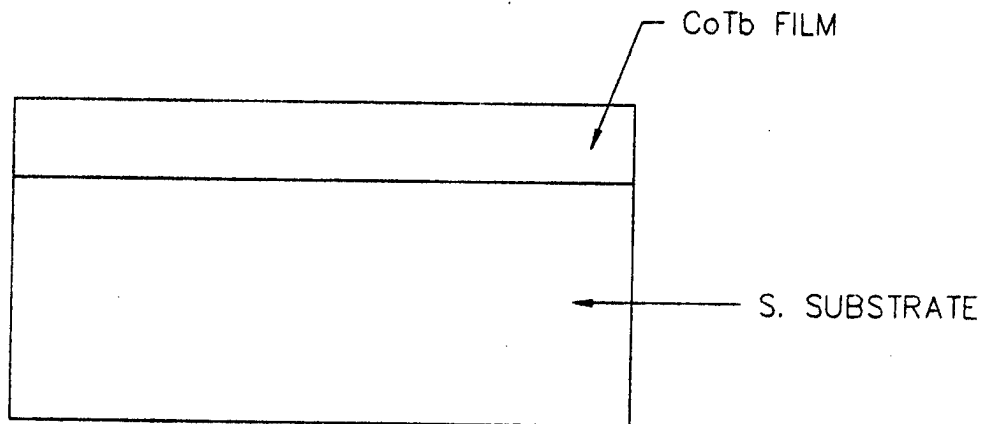


Figure 21

Such a structure can be fabricated by growing a of Co-Tb alloy using standard sputtering techniques. The substrate material should be extremely smooth such as Si waver or an Optical flat. Staufer et. al. have demonstrated the application of this material for writing bits in a write once read many application, in an ultra high vacuum environment.

b.3.2. Write/read times

Write/Erase

The write and erase times in the magnetic memory are limited by the current density from the microtip. Based on previous experiments by Kryder¹⁴ approximately 20 microwatts of power are required to melt the thin film. A 1 microamp current generated by a 2 volt potential will heat the thin film sufficiently.

Read

Reading the bits in the thermo-magnetic memory requires measuring the force between the magnetic dipole on a tip and the a magnetic dipole on the surface. The dipoles will be on the order of 500 angstroms in diameter. The apparatus for making these measurements is similar to the magnetic field microscope¹⁵. As discussed by Hartman¹⁶ experimental results obtained with magnetic force microscopes are not be predicted with standard assumptions. It is difficult to

¹⁴ H.D. Shiea, M. H. Kryder, Appl. Phys. Lett 49(8) 472, 1986.

¹⁵ Scanned Probe Microscopes, H. K. Wickramasinghe, Scientific American, October 1989.

¹⁶ U. Hartman, J. Appl. Phys., 64(3), 1561, 1989.

estimate the magnitude of the dipole - dipole force based on theoretical considerations.

As with the quantum structure memory, reading the data bits is achieved with a sensing device constructed from a microcantilever. The dimensions of the cantilever cannot be estimated until the dipole - dipole interaction forces are known.

b.3.3. Advantages/Disadvantages

There are several advantages and disadvantages to the electromagnetic substrate. The advantages include the use of materials and techniques developed already for the recording industry. Disadvantages include a lack of knowledge of the properties of magnetic domains that are smaller than .1 microns.

c. Conclusions of the Phase I Research

From this SBIR Phase I research project we conclude that it is feasible to create a read/write mass storage device using STM technology. Major conclusions of this study are:

1. Three promising substrates were evaluated as the storage medium for a read write mass storage device. The three approaches are a quantum structure substrate, an electrochemical substrate, and a thermo-magnetic substrate.
2. Of the three storage media studied the quantum structure and thermo-magnetic approaches are the most feasible.
3. The primary risk associated with building a mass storage device with STM technology is associated with a lack of knowledge of the behavior of devices and materials with dimensions of less than .1 micron.
4. It is estimated that progress on an STM based mass storage device will require a minimum of 10 man years of effort, more than twice the manpower available on the SBIR program.